

Short-range symmetry breaking induced structural collapse and T_c enhancement in 122-type iron pnictide superconductors

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In this paper, we investigate analytically the experimental observations of structural collapse and T_c enhancement in the rare earth-doped 122-type iron-based pnictide superconductors [S. R. Saha et.al. Phys. Rev. B **85**, 024525 (2012), arXiv:1105.4798 (2011); B. Lv et al. PNAS **108**, 15705 (2011).]. Based on the real-space effective c-axis lattice constant theory of superconductivity [X. Q. Huang, arXiv:1001.5067], it is shown that the abrupt c-axis reduction of the superconductors is due to the structural phase transition (an ultra-short-range symmetry breaking) of the charge stripe lattice. The existence of this phase transition corresponds to the change from the full-doped superconducting planes to the half-doped superconducting planes in the studied superconductors. It is estimated that this phase transition may help to promote the superconducting transition temperature of the 122 family up to as high as 80 K.

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I. INTRODUCTION

Twenty-six years after the discovery of high-temperature superconductivity in copper-based superconductors [1, 2], there is still ongoing debate about how charge carriers move to maintain the superconducting state in these materials [3, 4]. Since the discovery of iron-based superconductors [5], researchers have expected that the new superconductors may unlock the secrets of high-temperature superconductivity. However, after five years' intensive study in the iron-pnictide compounds [6–10], it seems that the condensed matter physics community has become more confused than ever. The researchers now find that they are unable to answer the following fundamental question: Do the cuprate and iron-based superconductors share an identical high-temperature mechanism of superconductivity? Though it has been widely believed that there is a remarkable possibility of an entirely different mechanism behind these two types of superconductors. We firmly believe that an exactly the same intrinsic physical reason is responsible for the superconductivity in both cases. Based on the quantum confinement effect and the minimum energy principle, we have proposed a unified description of cuprate and iron-based superconductivity [11].

The iron-based high-temperature superconductors started with the discovery of superconductivity at 26 K in the 1111-type $LaFeAsO_{1-x}F_x$ in 2008 [5], very soon, the superconducting transition temperature T_c was raised to 55 K by replacing the lanthanum with other rare-earth elements [6]. Fig. 1 shows the two typical families of the iron-based superconductors, they are 1111-type [5] of Fig. 1(a) and 122-type [8] of Fig. 1(b). Thus, facing the rapidly rising T_c , some researchers claimed that

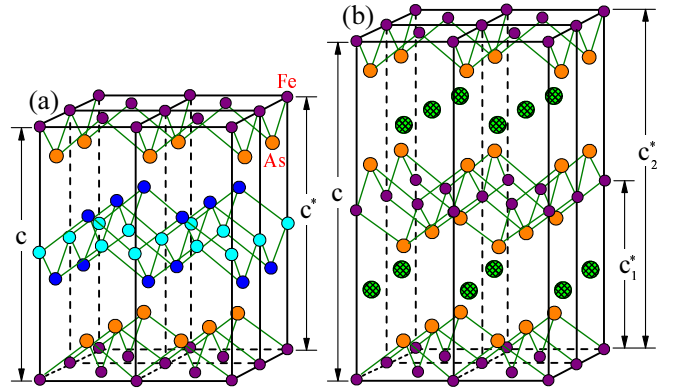


Figure 1: Two types of the iron-based superconductors. (a) The 1111-type with only single FeAs layer within one c-axis lattice constant, where the c-axis lattice constant c is equal to the effective c-axis lattice constant c^* . (b) The 122-type having two FeAs layers within the lattice constant c , in this case, there are two possible superconducting phases: the full-doped low T_c phase with the effective c-axis lattice constant $c_1^* = c/2$ and the half-doped high T_c phase of $c_2^* = c$.

room temperature superconductors made possible from the iron-based material. At almost the same time, we argued that the maximum T_c of the 1111 family cannot exceed 60 K, while the 122 family has a maximum $T_c^{\max} < 40$ K [11, 12]. So far, our first prediction is still true by a number of experiments tested in the past four years. But two different groups reported that the T_c of the rare earth-doped 122-type $CaFe_2As_2$ system can be dramatically enhanced to more than 45 K [13, 14], which breakthrough the limitation of 40 K given by our theory in 2008. Does this imply that our conclusion about the maximum transition temperature of the 122-type iron-based superconductors is false?

Recently, the pressure-induced T_c increase in $\beta - Fe_{1.01}Se$ compound was also observed [15].

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Most recently, the collapsed tetragonal phase of $Ca_{1-x}Pr_xFe_2As_2$ was confirmed by the NMR studies [16]. However, the nature of structural collapse and the high- T_c phase remains unclear. Here we will show that, in the framework of effective c-axis lattice constant theory of superconductivity [11], the experimental observations of structural collapse and T_c enhancement in 122-type iron pnictide superconductors can be well interpreted as a new ultra short-range symmetry breaking of the real-space charge stripes. In this picture, three different phase transitions (c-axis reduction, a-axis expansion and T_c enhancement) will occur simultaneously in the weak-doped 122-type superconductors. According to our theory, we conclude that the maximum superconducting transition temperature of the collapsed 122 family may be promoted to about 80 K.

II. WHAT IS THE KEY OF THE SUPERCONDUCTIVITY?

By now, many theories and models have been developed to explain the high-temperature superconductivity. As we all know, these theoretical works have not been accepted by the scholarly consensus [3]. We fully agree with Anderson that many theories about electron pairing in cuprate superconductors may be on the wrong track. In our opinion, these theoretical studies did not take into account the most essential point of the superconductivity. Then, what is the key of the high-temperature superconducting phenomena?

From the interaction point of view, any superconducting system can be simplified as a conventional classical electromagnetic interaction system between the negative electrons and positive ion cores. From the energy point of view, the superconducting state should be a stable condensation state of electrons which do not radiate electromagnetic energy. According to the classical electromagnetic theory, to maintain a non-dissipative superconducting electronic state, the corresponding superconducting electrons should not move with variable motion. In other words, each superconducting electron can be considered as the “inertial electron” on which the resultant force is zero.

In recent years, we have devoted considerable effort towards the development of a unified theory of superconductivity [11, 12, 17]. The new theory was established in the real-space picture, rather than the commonly used momentum-space picture in superconducting areas [19]. In our approach, the most basic unit of the superconducting ground state is the static one-dimensional charge chain (stripe) [18] formed in the ab-plane of the crystal lattice. Without the external field, it is not difficult to prove that the electrons will self-organize into some quantized one-dimensional peierls chains with $d + d' = b$ ($d > d'$), as shown in Fig. 2(a). Moreover, the real-space Cooper pair is defined within one single plaquette, as indicated in Fig. 2(a). Driven by the external fields,

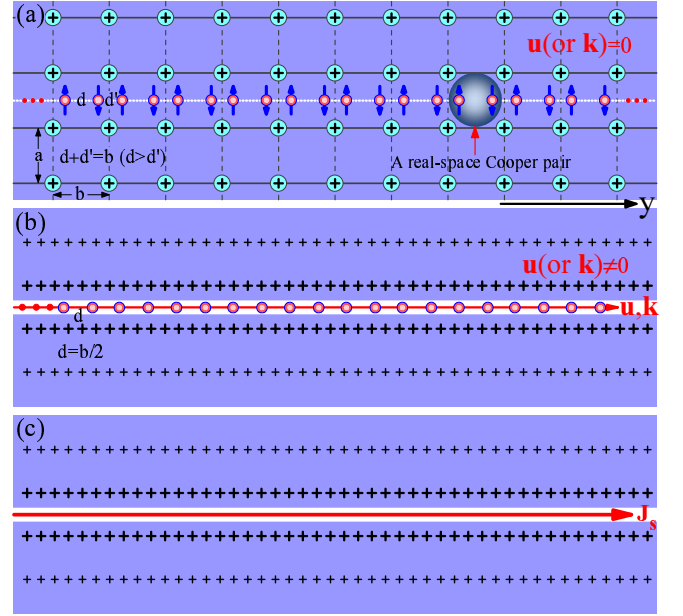


Figure 2: (a) The real-space superconducting ground state where the electrons self-assemble into some static one-dimensional peierls charge and spin antiferromagnetic stripes, the real-space Cooper pair can be formed inside single plaquette. (b) Under the influence of the external fields, the peierls chains will transfer into periodic chains and the electrons move at the same velocity u (or the same momentum k). (c) An equivalent model of (b), where the superconducting current can flow without resistance along the ballistic channel with a supercurrent density of J_s .

the ground state of the peierls chain will spontaneously transform into one superconducting excited state of a periodic chain with a definite electron-electron spacing of $d = b/2$, as illustrated in Fig. 2(b). It is obvious that all electrons are maintained in the zero-stress state and move constantly at the same velocity u (or in the same momentum k , which is differed from the BCS picture of opposite momentum required for the formation of the Cooper pairs [19].). The excited state of Fig. 2(b) can be equivalently described in term of superconducting persistent-current J_s , as indicated in Fig. 2(c).

For the three-dimensional layered superconductors (where the c-axis lattice constant $c > a$ and $c > b$), the charge stripes will undergo further self-assembly into some quasi-two-dimensional stripe lattices, as illustrated in Fig. 3. In this scenario, the superconducting current can flow without resistance along some periodic array of ballistic channels in the superconductor, as shown in Fig. 3(a) and (c). Due to the symmetry of the stripe lattices [see Fig. 3(b) and (d)], the stripe-stripe electromagnetic interactions can be naturally suppressed to ensure the stable superconducting state. In Fig. 3(b) and (d), the parameter c^* is the so-called effective c-axis lattice constant in our theory. Normally, the parameter c^* is taken to be the lattice constant c of the superconducting crystal. However, it may also be equal to $c/2$ in some special

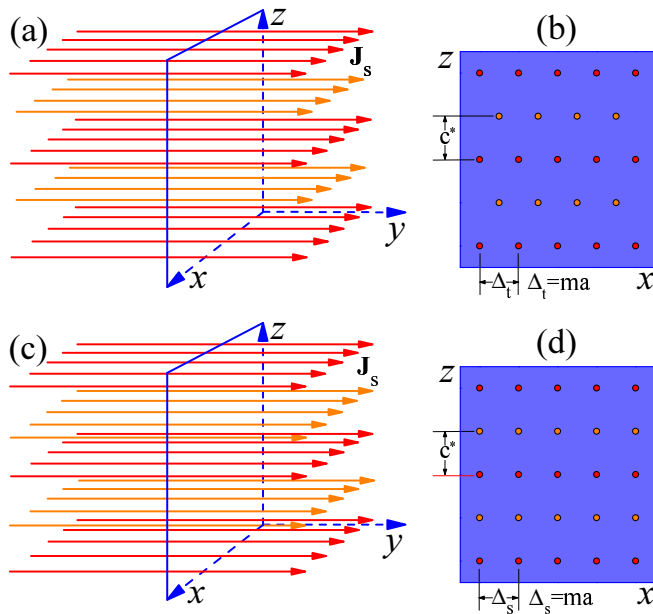


Figure 3: The quasi-two-dimensional charge stripe lattices of different symmetries. (a)-(b) triangle or equilateral triangle, (c)-(d) rectangular or square, where a is the a-axis lattice constant, c^* is the effective c-axis lattice constant defined in our theory and m is a positive integer.

cases. In the following, we will show that the parameter c^* plays a main role in determining the maximum T_c of a given superconductor.

III. THE MAXIMUM T_c AND THE EFFECTIVE C-AXIS LATTICE CONSTANT

It is our view that a successful theory of superconductivity can not only explain the observed experiments, but it can also predict new phenomena and give a clear physical description of the predicted results. For a given superconducting material, perhaps the most difficult to answer is: What is the highest superconducting transition temperature expected for the superconductor? To the best of our knowledge, the real-space effective c-axis lattice constant theory of superconductivity can be considered as the first one that successfully estimate the maximum T_c of the studied compound.

In the framework of the lattice model of charge stripe (see Fig. 3), the superconducting transition temperature of a superconductor is closely related to the stability of the stripe lattice inside the materials. In our theoretical model, the lattice vibrations always have the tendency to destroy the existing superconducting state of the stripe lattice. This implies that the BCS electron-phonon coupling is probably not the cause of the superconductivity and the pairing mechanism [20]. Furthermore, we consider that the stripe-stripe electromagnetic interaction is one of the most important factors that affects the stability of the stripe lattice, in turn, influence the maximum

T_c of the corresponding superconductor. Qualitatively, a too strong stripe-stripe interaction could lead to a lower T_c in the superconductor. Obviously, in order to promote the T_c of the superconductor, it is necessary to control the Coulombic stripe-stripe interaction to an optimum value.

With the help of Fig. 3, the most bewildering problem of superconductivity in layered superconductors is no longer mysterious. Now, the superconducting state is related simply to the ordered charge structure due to the competition among the electrons. Because of the intrinsic Coulomb repulsion between superconducting stripes, a superconducting state in fact is an energy state with a condensed electromagnetic energy which is called superconducting internal energy (SIE) in this paper. In the following, we briefly discuss the relationship among the SIE, the maximum T_c and the lattice parameters of the studied superconductor. Without losing the generality, we focus our discussion on the striped triangular lattice of Fig. 3(b). In the first approximation, the SIE can be expressed directly as

$$E_{SIE} = \frac{A(n, T)}{c^*} + \frac{B(n, T)}{ma}, \quad (1)$$

where n is the concentration of charge carriers (electrons), T is the temperature, $A(n, T)$ and $B(n, T)$ are n and T related constants, the parameters c^* , a and m are given in Fig. 3.

It must be pointed out that Eq. (1) is not suitable for the following four extreme systems: (a) n is too small, (b) c^* is too large, (c) n is too large and (d) c^* is too small. For the cases (a) and (b), the competitive interaction between electrons is too weak to form the ordered superconducting stripe lattice. While for the cases (c) and (d), the stripes are crowded and the stripe-stripe interactions are too strong to allow a stable stripe lattice.

In our theoretical framework, for the doped high-temperature superconducting materials, researchers can adjust the crystal structure of stripe lattices by changing the electron concentration n , and thus alter the internal energy E_{SIE} and the superconducting transition temperature T_c . Based on the relationship between symmetry and stability of the system, the optimal doped sample corresponds to the minimum energy of the stripe structure with regular triangle ($c^* = 0.5\sqrt{3}\Delta_t$) or square ($c^* = \Delta_s$) symmetry of Fig. 3. Hence, for a high-temperature superconductor with an effective c-axis lattice constant c^* , there exists a simple relation between c^* and the minimum internal energy E_{SIE}^{min} :

$$E_{SIE}^{min} \propto \frac{1}{c^*}. \quad (2)$$

Here, the stripe lattice with the minimum energy E_{SIE}^{min} corresponds to the maximum T_c^{max} of a superconducting state. The T_c^{max} and E_{SIE}^{min} satisfy the following relation:

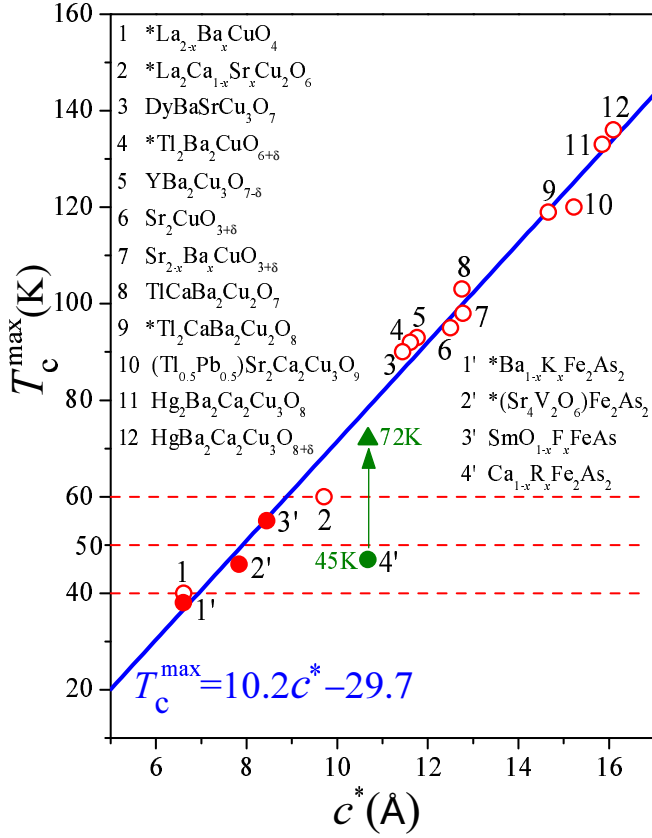


Figure 4: The linear relationship between the measurements maximum T_c and the effective c-axis lattice constant c^* of Cu- and Fe-based high-temperature superconductors. The blue line is obtained by fitting the experimental data of copper superconductors (the hollow circles). Here, the materials marked by “*” are those of $c^* = c/2$, while the other satisfy $c^* = c$. The green solid circle of 45 K is the experimental value of collapsed $Ca_{0.92}Nd_{0.08}Fe_2As_2$ sample and the triangle of 72 K is the expected value also from the experiment of Saha et al. [13].

$$T_c^{max} = A + \frac{B}{E_{SIE}^{min}} = A + Bc^*, \quad (3)$$

where A and B are two constants which can be determined experimentally.

It can be concluded from Eq. (3) that increasing the effective c-axis lattice constant c^* is the most effective way to raise the maximum superconducting transition temperature of the high-temperature layered superconductors. This conclusion is well confirmed by a large number of experimental results reported for the cuprate and iron-based superconductors, as shown in Fig. 4. In this figure, the qualitative result of linear relationship of Eq. (4) between T_c^{max} and c^* is clearly shown. It should be noted that the fitted line is obtained with the fitting parameters of cuprate superconductors (marked by twelve hollow circles) and the corresponding equation is written as:

$$T_c^{max} \approx -29.7 + 10.2 \times c^*. \quad (4)$$

By comparing Eq. (4) with Eq. (3), the intercept and slope of Eq. (3) are $A \approx -29.7$ and $B \approx 10.2$, respectively. Furthermore, we note that the experimental data of the 1111-, 21311- and 122-type iron-based superconductors also fall on this line, as indicated by three solid circles in Fig. 4. Based on this surprising result, we have hypothesized that the maximum T_c of the 1111-, 21311- and 122-type iron-based superconductors cannot exceed 60 K, 50 K and 40 K (indicated by the dotted red lines in Fig. 4), respectively. However, as pointed out in the abstract, the limitation of 40 K has recently broken through in the rare earth-doped 122-type $CaFe_2As_2$ systems [13, 14]. In the next section, we will give an interpretation of these new experimental results.

IV. STRUCTURAL COLLAPSE AND T_c ENHANCEMENT IN 122-TYPE IRON-BASED SUPERCONDUCTORS

Why the structural collapse in 122-type family of iron pnictides can result in a sharp increase of the T_c value in the corresponding samples? This question not only challenges the traditional understanding of superconductivity, but also challenges our conclusion that the maximum T_c of the 122-type parent compounds cannot exceed 40 K. In this section, we show that the new experimental facts mentioned above are the desirable results in our framework and they can be well explained within the effective c-axis lattice constant theory of superconductivity.

According to our theory, an abrupt change of the superconducting transition temperature is always associated with a radical change in the effective c-axis lattice constant of the superconductor. Hence, in order to explain the new phenomenon of T_c enhancement one should start from the lattice structure of Fig. 1(b), especially the change of the effective c-axis lattice constant. Different from the FeAs-1111 phase of Fig. 1(a), there are two superconducting FeAs layers within one lattice constant c in the FeAs-122 phase. So in the 122-type family, there exist two different superconducting phases. The first one is the full-doped phase where all the FeAs layers are doped and contribute to the superconductivity, in this case, the corresponding effective c-axis lattice constant satisfies $c_1^* = c/2$, while the second one is the half-doped phase where the FeAs layers doped interval with $c_2^* = c$, as indicated in Fig. 1(b). Since $c_2^* > c_1^*$, so the half-doped phase naturally has a higher T_c^{max} than that of the full-doped phase.

Now the key issue is how to get the half-doped 122-type superconducting samples in laboratory. Intuitively, a heavily doped (high carrier concentration) sample tends to be in the half-doped phase, while the light doped (low carrier concentration) sample may exist in the half-doped

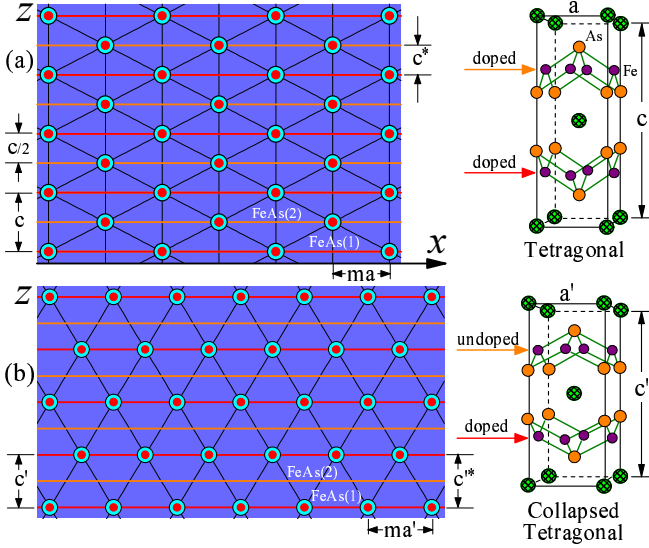


Figure 5: The real space full-doped to half-doped charge-stripe phase transition in the weak-doped 122-type FeAs superconductors. (a) The uncollapsed full-doped phase, (b) the collapsed half-doped phase. This phase transition will lead directly to the c-axis reduction ($c' < c$), a-axis expansion ($a' > a$) and at the same time T_c enhancement in the corresponding sample.

structural state. These model predictions are consistent with the experimental results, which indicated that the T_c enhancement occurs only at doping concentration $< 16\%$. Next, we will present a detailed analysis of the reported new physical phenomena by applying our approach to the 122-type compounds.

In 122-type FeAs superconductors, there are two sets of FeAs layers which are FeAs(1) set and FeAs(2) set as illustrated in red and orange lines respectively in Fig. 5. As can be seen from this figure, the FeAs(1)-FeAs(1) or FeAs(2)-FeAs(2) spacing equals to the lattice constant c , while FeAs(1)-FeAs(2) spacing is $c/2$. Generally, both FeAs(1) and FeAs(2) layers are doped with charge carriers and all FeAs layers are in the superconducting phase, as shown in Fig. 5(a). In the absence of the external pressure, the charge carriers (electrons) may enter into all FeAs layers and self-assemble into a metastable full-doped phase. In this case, the corresponding effective c-axis lattice constant is $c^* = c/2$ implying a relatively small T_c^{max} in this sample. However, when a pressure is applied to the sample, the FeAs(1)-FeAs(2) spacing will decrease with the increase of pressure. The shrinking of the spacing in turn could result in a great increasing of the layer-layer interaction, while decreasing the instability of the lattice crystal and superconducting stripe lattice.

When the applied pressure exceed the critical point, two structural phase transitions of the crystal structure and stripe lattice structure will happen simultaneously, as shown in Fig. 5(b). This is the so-called full-doped to half-doped real space phase transition which is driven by

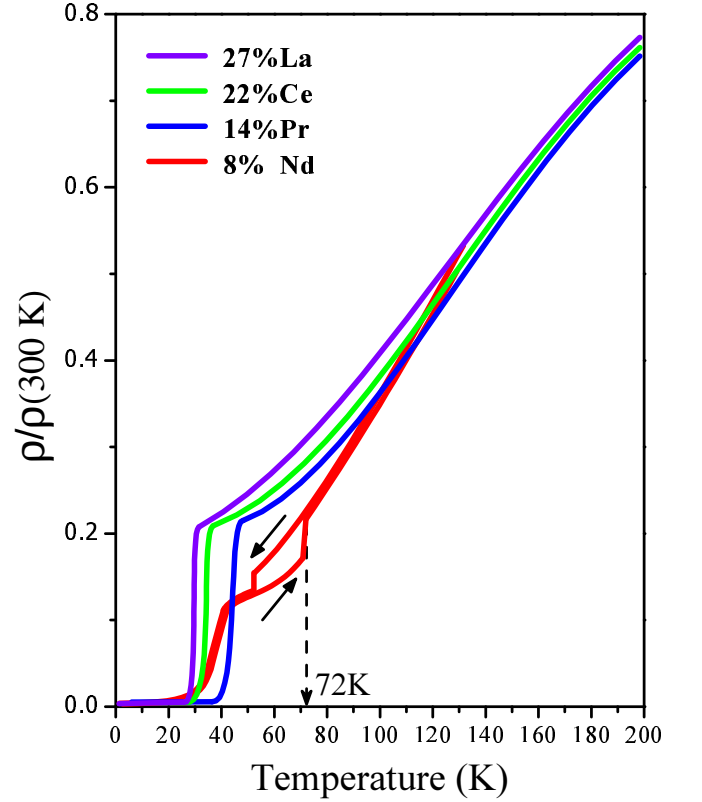


Figure 6: The experimental results from Fig. 12 of Ref. [13] by Saha et al. For the weak-doped sample of $Ca_{0.92}Nd_{0.08}Fe_2As_2$, the corresponding superconducting transition temperature near 45 K (the red line), the expected maximum T_c^{max} is about 72 K indicated by the dashed arrow.

an external pressure. As we can see from Fig. 5, these phase transitions are closely related with the migration of electrons from FeAs(2) layers to FeAs(1) layers, which can further be viewed as an ultra short-range symmetry breaking of the stripe lattice. This symmetry breaking will lead directly to the following observable changes: (1) a dramatically abrupt c-axis contraction ($c \rightarrow c'$, where $c/2 < c' < c$) because of the decreasing of doped layer-layer interaction ($c/2 \rightarrow c'$); (2) a significant a-axis expansion ($a \rightarrow a'$, where $a < a'$) due to the increasing of in-plane stripe-stripe interaction ($2ma \rightarrow ma'$); (3) an obvious enhancement of T_c originated from the increase of effective c-axis lattice constant [$c^* (= c/2) \rightarrow c'^* (= c')$]. These qualitative analysis results are identical with the recent experimental results [13, 14, 21].

According to the results of the previous section and the experimental reported lattice constants [13], it is possible to quantitatively estimate the maximum T_c^{max} in the collapsed 122-type iron-based superconductors. In the paper [13], the authors synthesized a series of doped 122-type samples of different elements and different concentrations, among which the sample $Ca_{1-x}Nd_xFe_2As_2$ with x around 0.09 was studied in detail. The crystallographic data for this sample are ($a = 3.9202\text{ \AA}$,

$c = 11.273\text{\AA}$) and ($a' = 3.92822\text{\AA}$, $c' = 10.684\text{\AA}$) for the tetragonal structure and the collapsed tetragonal structure, respectively. Moreover, the collapse transition temperature is around 80 K with the uncertainty in temperature values being ± 5 K. Consequently, the effective c-axis lattice constant of the collapsed sample is $c'^* = c' \approx 10.684\text{\AA}$, and then we can get the corresponding maximum $T_c^{max} \approx 79.3$ K by putting the c'^* value into Eq. (4). Note that this theoretical value of T_c^{max} is in complete coincidence with the collapse transition temperature of 80 K, however, is much higher than the experimental result of $T_c = 45$ K for $Ca_{0.92}Nd_{0.08}Fe_2As_2$, as shown in the red line in Fig. 6. We believe that the difference between theory and experiment might be due to the quality of the samples as well as to the non-optimal doping concentration. In fact, from Fig. 6 there is a clear evidence that superconducting phase transition is most likely to occur at about 72 K which is very close to the idea value of 79.3 K (see also Fig. 4), as indicated in the dashed arrow in the figure.

V. A BRIEF SUMMARY AND CONCLUSIONS

Based on the real-space effective c-axis lattice constant theory of superconductivity, we have studied the

recent experimental findings of structural collapse and T_c enhancement in the rare earth-doped 122-type iron-based pnictide superconductors. We have argued that the abrupt c-axis reduction of the superconductors is due to the full-doped to half-doped structural phase transition (an ultra-short-range symmetry breaking) of the charge stripe lattice. It has been shown that phase transition directly leads to the expansion of effective c-axis lattice constant, which in turn enhance the maximum superconducting transition temperature of the studied materials. According to the experimental crystallographic data, it has been estimated that the T_c of the collapsed 122 family can be raised to as much as 80 K by improving the quality of single crystal component and by adjusting the carrier concentration inside the superconductor. We have pointed out that the three phase transitions (c-axis reduction, a-axis expansion, and T_c enhancement) observed in weak doped 122 series are intrinsically correlated. In this paper, the physical nature of the new experimental findings has been understood quite well on the basis of our approaches, which implies that our framework may provide further insight into the mechanism of the high-temperature superconductivity in general.

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